

Materials and Manufacturing Challenges of Direct Methanol Fuel Cells

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INTRODUCTION

Fuel cells are attractive power sources for a variety of Department of Defense (DoD) needs. Among the various types of fuel cells, direct methanol fuel cells (DMFC) are particularly well-suited for mobile applications (such as soldier power, unmanned underwater systems, and communication devices) since DMFCs employ easily manageable liquid methanol fuel with excellent energy storage densities. The use of DMFCs for portable devices will eliminate the lengthy recharging process required for lithium ion (Li-ion) batteries (using an electrical outlet). [1] DMFCs provide uninterrupted, continuous power as long as the methanol fuel is supplied since they are energy conversion devices rather than energy storage devices, such as batteries. Moreover, DMFCs provide a much higher energy density than Li-ion batteries. Theoretically, methanol offers a volumetric energy density and a gravimetric (weight) energy density that is ten and 30 times higher, respectively, than Li-ion batteries. However, in practice the energy density of DMFCs will be lower than the theoretical value due to their lower efficiency (approximately 30 %). Nevertheless, use of a DMFC can reduce the weight of the power supply by 50% when running a 20 watt (W) laptop for 24 hours. The reduction in power supply weight increases as the system size increases due to the decoupling of power delivery from energy storage. For example, a DMFC can reduce the weight of power sources soldiers need to carry by up to 65% over a 72-hour mission. [2]

However, the adoption of DMFC technology has been hampered by high system costs and complexity, low operating voltage and efficiency, and durability issues. [1] Several of these problems are directly linked to materials, manufacturing, and system challenges. This article focuses on the materials and manufacturing challenges and the development of new materials to overcome these technical problems, thus making DMFC technology viable for the DoD and consumer applications.

DIRECT METHANOL FUEL CELLS

The principles involved in the operation of a direct methanol fuel cell are shown in Figure 1. A DMFC consists of an anode, a cathode, and a proton-conducting electrolyte membrane, which are collectively called a membrane-electrode assembly (MEA). Conventionally, the anode and cathode catalysts are, respectively, nanostructured platinum-ruthenium (Pt-Ru) and Pt particles (approximately 3 nm) dispersed in a conductive carbon support.

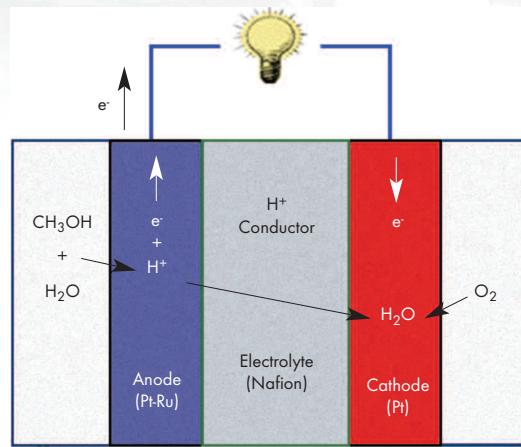


Figure 1. Operating principles of a direct methanol fuel cell (DMFC).

The proton-conducting electrolyte normally employed is a polymeric membrane called Nafion®,* which is a hydrated perfluorosulfonic acid polymer (see Figure 2). During the cell operation, protons are produced by an oxidation of methanol fuel with the

assistance of the Pt-Ru electrocatalyst at the anode. The produced protons migrate from the anode into the cathode through the Nafion membrane, while the electrons produced during the oxidation reaction flow from the anode to the cathode through the external circuit, as indicated in Figure 1. The electrons and protons react with the diatomic oxygen molecules at the cathode with the assistance of the Pt electrocatalyst to produce water as the byproduct. The relevant chemical reactions occurring at the anode and cathode as well as the overall cell reaction are given in Figure 3. The free energy change, ΔG , involved with the overall chemical

reaction is tapped out as useful electrical energy in accordance with the relation below:

$$\Delta G = -nFE \quad (1)$$

where n is the number of electrons involved in the chemical reaction, F is the Faraday constant (96,487 coulombs per mole), and E is the cell voltage. The single cells similar to the one shown in Figure 1 are stacked together with carbon bipolar plates to obtain a fuel cell stack which can provide the desired voltage and power.

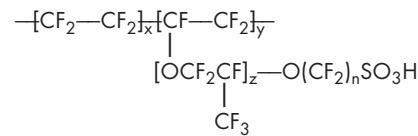


Figure 2. Chemical structure of the polymeric membrane Nafion.

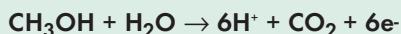
MATERIALS CHALLENGES

The performance and commercialization of DMFCs is, however, hampered by problems associated with the polymeric Nafion membrane, Pt and Pt-Ru electrocatalysts, and carbon support. The materials challenges are briefly outlined in this section.

The use of Nafion as a membrane in DMFC presents several difficulties. [3] First, it is expensive. Second, Nafion allows permeation of methanol fuel from the anode to the cathode, generally referred to as *methanol crossover*. This is important because oxidation of the permeated methanol on the cathode Pt electrocatalyst leads to mixed potentials at the cathode, resulting in voltage loss. The methanol permeation also results in a waste of fuel and con-

Report Documentation Page			Form Approved OMB No. 0704-0188	
<p>Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p>				
1. REPORT DATE 01 JAN 2009	2. REPORT TYPE N/A	3. DATES COVERED -		
4. TITLE AND SUBTITLE Materials and Manufacturing Challenges of Direct Methanol Fuel Cells			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Manthiram, A			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Texas at Austin, Austin, TX			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Defense Technical Information Center, Ft Belvoir, VA			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited				
13. SUPPLEMENTARY NOTES The original document contains color images.				
14. ABSTRACT Fuel cells are attractive power sources for a variety of Department of Defense (DoD) needs. Among the various types of fuel cells, direct methanol fuel cells, direct methanol fuel cells (DMFC) are particularly well-suited for mobile applications (such as soldier power, unmanned underwater systems, and communication devices) since DMFCs employ easily manageable liquid methanol fuel with excellent energy storage densities.				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 6
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	19a. NAME OF RESPONSIBLE PERSON	

Reaction at the anode:



Reaction at the cathode:



Overall cell reaction:



Figure 3. Chemical reactions involved in a direct methanol fuel cell (DMFC).

offers an increase in ionic resistance and a decrease in power density.

Methanol permeability and crossover occur due to the structure of the Nafion membrane. Nafion consists of hydrophobic main chains and hydrophilic side chains containing ionic sulfonic acid ($-\text{SO}_3\text{H}$) groups, as shown in Figure 2. The sulfonic acid groups cluster together to form ionic channels, as illustrated in Figure 4. While the flow of water through the ionic channels helps to carry the protons (vehicle mechanism of proton conduction) and offers high proton conductivity, it also leads to a flow of methanol from the anode to the cathode. The formation of wider ionic channels facilitated by the aliphatic polymeric structure of Nafion leads to a high crossover of methanol from the anode to the cathode. Moreover, the Nafion fluoropolymer membrane is prone to attack by peroxide and superoxide intermediates formed during the oxygen reduction reaction. These drawbacks have generated immense interest in the development of alternative membranes for DMFCs.

As shown in Figure 3, the methanol oxidation reaction involves a six-electron process, while the oxygen reduction reaction involves a four-electron process. The higher energy required to break the carbon-hydrogen bonds and the six-electron process make the methanol oxidation reaction sluggish even with the best known Pt-Ru electrocatalyst. Similarly, the difficulty in breaking the double bonds of the diatomic oxygen molecule and the four-electron process make the oxygen reduction reaction also slow even with the best known electrocatalyst (Pt). Both the sluggish methanol oxidation and oxygen reduction reactions lead to a significant drop in the cell voltage of a DMFC under the operating conditions. The oxygen reduction reaction is a common process for both DMFCs and proton exchange membrane fuel cells (PEMFCs) operating with hydrogen fuel. However, the much slower oxidation of methanol in DMFCs, compared to that of hydrogen in PEMFCs, together with a poisoning of the cathode Pt electrocatalyst[†] results in a low operating voltage for a DMFC compared to that of a PEMFC.

Although Pt is used for the oxidation of hydrogen fuel in a PEMFC, Pt-Ru rather than Pt is used to oxidize methanol fuel in a DMFC. The addition of Ru oxidizes the carbon monoxide

sequently a reduction in energy density. To reduce methanol crossover, thicker membranes like Nafion-117 (175 μm thick) are often preferred for DMFC. This

(CO) intermediate formed during the methanol oxidation reaction to carbon dioxide (CO_2) through the formation of hydroxyl groups.[4] However, the use of Pt-Ru brings additional difficulties, since Ru tends to migrate as a dissolved species from the anode to the cathode through the Nafion membrane. The gradual depletion of Ru at the anode during DMFC operation leads to a decrease in the kinetics of the already slow methanol oxidation reaction and consequent performance loss. Also, the electrocatalysts at the cathode and anode tend to dissolve and reform, resulting in an increase in particle size and consequent decrease in electrocatalytic activity and performance during cell operation.[5]

The electrocatalysts are normally employed as supported catalysts, (i.e. the electrocatalysts are dispersed in a conductive carbon support) and the carbon-supported Pt-Ru/C and Pt/C electrocatalysts are employed, respectively, as anode and cathode in a DMFC. While the electrolyte membrane should support only ionic (proton) conduction without any electronic conduction, the anode and cathode should support both proton and electron conduction to allow the flow of protons and electrons. The mixed ionic-electronic conduction in the electrodes is generally achieved by adding an adequate amount of the ionomer Nafion into the carbon-supported anode and cathode structures. The dispersion and distribution of the electrocatalysts and the ionomer in the conductive carbon support are critical to efficiently utilize the expensive Pt-based electrocatalysts. Any electrocatalyst nanoparticles trapped in the micropores of the carbon support cannot be accessed by the methanol fuel or the oxygen oxidant. Approximately 70% of the electrocatalysts in the electrode structure often become unutilized, resulting in a waste of the expensive electrocatalysts. Moreover, the porous carbon structure is prone to corrosion and degradation under the operating conditions of temperature and potential, which causes performance loss during long-term operation.

Some of the critical materials challenges that are discussed above are summarized here:

- High cost of Nafion membrane and Pt-based electrocatalysts
- High methanol permeability and crossover of methanol through the Nafion membrane
- Degradation of Nafion membrane by peroxide and superoxide intermediates formed during reaction
- Sluggish methanol oxidation reaction on the Pt-Ru electrocatalyst
- Sluggish oxygen reduction reaction on the Pt electrocatalyst
- Dissolution and growth of the electrocatalyst particles during cell operation
- Poisoning of the cathode Pt electrocatalyst by the permeated methanol
- Trapping of electrocatalysts in the micropores of carbon and their resultant poor utilization
- Chemical instability and corrosion of the carbon support

These critical challenges have created enormous interest in the development of alternate membranes, electrocatalysts, and conductive supports for DMFCs. Accordingly, a brief overview of the development of new membranes and electrocatalysts that can overcome some of the problems is presented below.

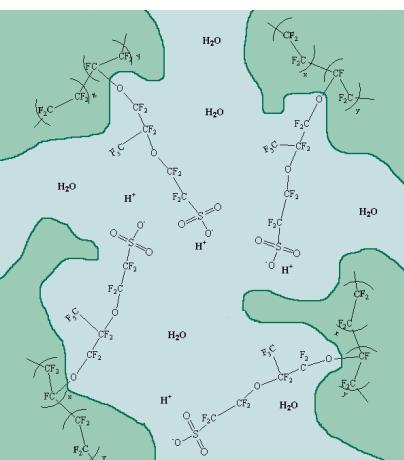


Figure 4. Formation of ionic channels by a clustering of the sulfonic acid groups in a polymeric Nafion membrane.

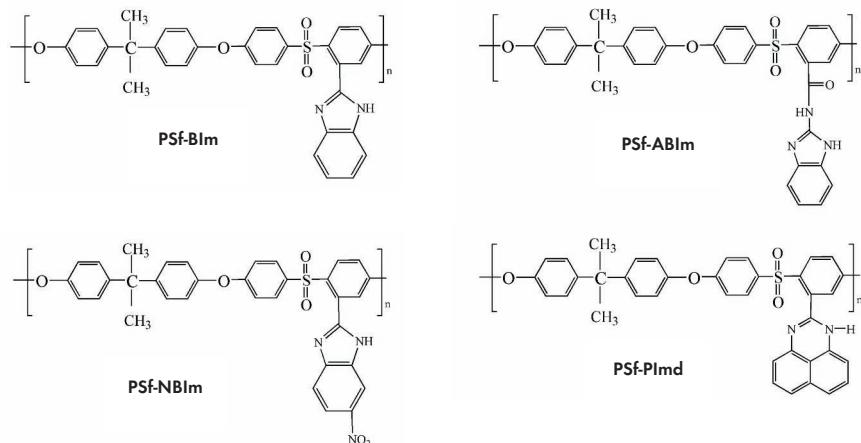


Figure 5. Structures of various N-heterocycles tethered to basic aromatic polymers.

NEW MATERIALS DEVELOPMENT

Membranes

With a given membrane thickness, aromatic polymers such as sulfonated poly(ether ether ketone) (SPEEK) and sulfonated poly(sulfone) (SPSF) are known to exhibit lower methanol crossover than Nafion.[6-8] The lower methanol crossover is due to narrower ionic channels compared to that in Nafion as indicated by small angle X-ray scattering.[9] While the flexible aliphatic chains facilitate the formation of wider ionic channels in Nafion, the less flexible aromatic backbones in SPEEK and SPSF lead to narrower ionic channels. However, SPEEK and SPSF membranes exhibit lower proton conductivity than Nafion. In recent years research has been focusing on blend membranes consisting of an acidic polymer and a basic polymer which have similar aromatic backbones.[10-14] The approach involves the tethering of an N-heterocycle group to an aromatic polymer like poly(sulfone) (PSf) or poly(ether ether ketone) (PEEK) to obtain a basic polymer, followed by its blending with an aromatic acidic polymer such as SPEEK or SPSF. Figure 5 shows four basic polymers in which benzimidazole (BIm), amino-benzimidazole (ABIm), nitrobenzimidazole (NBIm), and perimidine (PIIm) have been tethered to PSf to give, respectively, PSf-BIm, PSf-ABIm, PSf-NBIm, and PSf-PIIm. In a

blend membrane consisting of one of these basic polymers and the acidic polymer SPEEK, the acid-base interaction between the nitrogen atoms of the basic polymer and the sulfonic acid groups of the acidic polymer provides proton conduction via a Grotthuss-type (hopping of protons) mechanism, as illustrated in Figure 6. This is in addition to the vehicle mechanism that occurs between the sulfonic acid groups of the acidic polymer utilizing water as a proton transport medium similar to that in Nafion. Due to the occurrence of both vehicle and Grotthuss-type mechanisms, these blend membranes exhibit higher proton conductivity than the acidic polymer SPEEK itself (Table 1) at optimum acidic to basic polymer ratios.

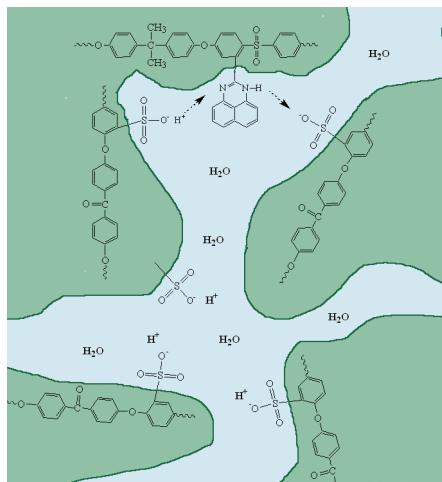


Figure 6. Formation of ionic channels by a clustering of the sulfonic acid groups and an insertion of the basic N-heterocycle groups into the ionic channels due to acid-base interaction in the blend membranes.

Although the conductivity values of the blend membranes are still lower than that of Nafion, the blend membranes with a thickness of approximately 60 μm exhibit significantly lower methanol crossover than Nafion-115 (125 μm thick) and SPEEK (approximately 60 μm thick) membranes, as displayed in Table 1. The methanol crossover value of Nafion-117 is similar to those of the blend membranes, but the much thicker (175 μm) Nafion-117 membrane will encounter higher ionic resistance. As a result, the blend membranes exhibit

lower voltage loss and higher power density than Nafion-115, Nafion-117, and SPEEK membranes (Figure 7 and Table 1). In

Table 1. Comparison of the open-circuit voltage (OCV), proton conductivity at 65°C and 100% relative humidity, maximum power density, and methanol crossover current density of Nafion-115 (125 μm thick), Nafion-117 (175 μm thick), plain SPEEK (approximately 60 μm thick), and blend membranes with different basic polymers (approximately 60 μm thick). The cell temperature is 65°C and the methanol feed concentration is 1 mol/dm³.

Membrane	OCV (V)	Maximum power density (mW/cm ²)	Methanol crossover current density (mA/cm ²)	Proton conductivity (mS/cm)
Nafion-115	0.63	59	122	143
Nafion-117	0.71	49	86	143
SPEEK	0.69	64	115	69
SPEEK/PSf-ABIm	0.71	95	95	94
SPEEK/PSf-NBIm	0.73	84	87	87
SPEEK/PSf-BIm	0.72	73	91	79
SPEEK/PSf-PIIm	0.74	73	77	73

fact, the lower methanol crossover of the blend membranes enables us to work with much thinner membranes compared to Nafion-115 and Nafion-117, which helps to overcome the lower proton conductivity limitations of the SPEEK or the blend membranes.

As shown in Table 1, the lower methanol crossover with the blend membranes is reflected in higher open-circuit voltages (OCV) compared to those found with SPEEK and Nafion-115 membranes. The lower methanol crossover can also allow operation of DMFCs with higher concentrations of methanol, offering the possibility to enhance the energy density of practical DMFC systems.[13] The lower methanol crossover of the SPEEK membrane compared to that of Nafion-115 membrane is due to the narrower ionic channels as pointed out earlier.[6-9] The lower methanol crossover of the blend membranes compared to that of SPEEK membrane itself is due to the insertion of the N-heterocycle groups into the ionic cluster, as shown in Figure 6. This was confirmed by small angle X-ray scattering studies. Both the lower methanol crossover and the enhanced proton conductivity lead to a better performance for the blend membranes compared to the conventional SPEEK membrane with the same thickness (approximately 60 μm).

The blend membrane strategy presented here has the potential to improve the performance further by optimizing the pKa value difference between the acidic and basic polymers as well as by tethering different N-heterocycles in the basic polymer. One critical issue with these new membranes is to employ a compatible ionomer in the electrocatalysts layer and thereby minimize the interfacial resistance between the membrane and electrocatalyst layers. Accordingly, the membrane-electrode assemblies fabricated with the blend membranes and SPEEK ionomer in the catalyst layer offer better performance than MEAs fabricated with the blend membranes and Nafion ionomer.[15]

In addition to offering attractive performance in DMFCs, these blend membranes are inexpensive compared to the fluoropolymer Nafion. The components in the blend membranes are also known to exhibit excellent chemical, thermal, and mechanical stabilities. With lower cost and interesting performance, the blend membranes described here offer great promise for DMFC applications.

Electrocatalysts

As pointed out earlier, carbon-supported Pt-Ru and Pt (designated as Pt-Ru/C and Pt/C) are the best known electrocatalysts, respectively, for the methanol oxidation and oxygen reduction reactions.

Recent research at the University of Texas at Austin has been focusing on Pd-based electrocatalysts for the oxygen reduction reaction. The oxygen reduction reaction involves the adsorption of O_2 molecules on the electrocatalyst, followed by a cleaving of the O-O bond and reduction of the metal oxide with H^+ ions to produce water (see cathode reaction in Figure 3). With this perspective,

alloying of a metal like palladium (Pd), which has high positive electrochemical reduction potential, E° , with another metal like cobalt (Co), which has high negative free energy change ΔG for oxide formation, has been considered to offer high electrocatalytic activity for the oxygen reduction reaction.[16] Accordingly, several Pd-based alloys such as Pd-Co, palladium-molybdenum (Pd-Mo), and palladium-tungsten (Pd-W) have been explored as electrocatalysts for oxygen reduction reaction.[17-21] The incorporation of Co, Mo, and W with high negative ΔG for oxide formation into Pd invariably enhances the electrocatalytic activity. More importantly, alloying of Pd with other metals increases the chemical stability and durability and inhibits the particle growth on annealing at higher temperatures.[19-21]

The Pd-based alloys exhibit much higher tolerance to methanol than Pt. This offers an important advantage in DMFCs as the Pd-based electrocatalysts will be poisoned to a lesser extent than Pt by the methanol that permeates from the anode to the cathode through the membrane, and thereby minimizing the voltage or performance loss. Figure 8 compares the performances of commercial Pt/C and $\text{Pd}_4\text{Co}/\text{C}$ electrocatalysts for the oxygen reduction reaction. With a thicker Nafion-115 membrane (125 μm thick) and high catalyst loading (1.0 mg/cm^2), commercial Pt/C exhibits higher catalytic activity (or lower voltage loss) than $\text{Pd}_4\text{Co}/\text{C}$, while with a thinner Nafion-112 membrane (50 μm thick) and a low catalyst loading (0.3 mg/cm^2), $\text{Pd}_4\text{Co}/\text{C}$ exhibits performance similar to that of commercial Pt/C. Although the intrinsic catalytic activity of Pd_4Co is lower than that of Pt, when the methanol crossover is high with the thinner Nafion-112 membrane and the catalyst loading is low, a higher poisoning effect of the Pt electrocatalyst by methanol compared to that of Pd_4Co brings down the performance of Pt similar to that of Pd_4Co . The higher tolerance of Pd-based

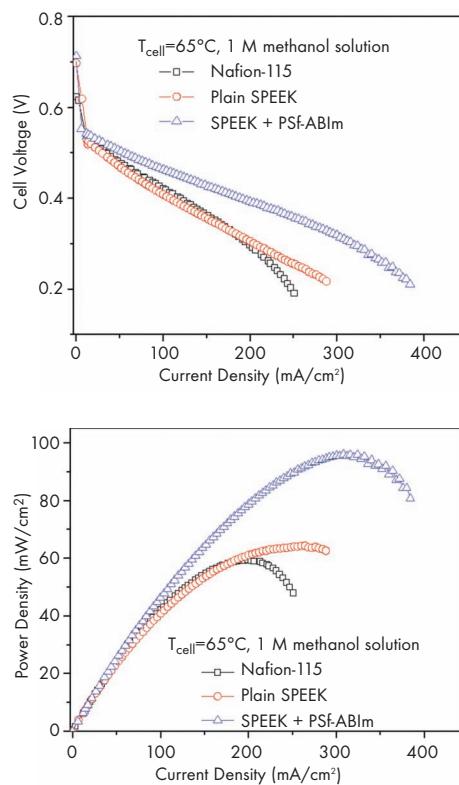


Figure 7. Comparison of the polarization curves and power densities of the blend membrane consisting of acidic SPEEK and basic PSf-ABIm polymers with those of Nafion-115 and SPEEK membranes.

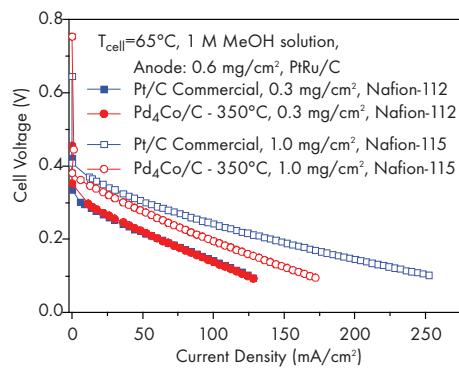


Figure 8. Comparison of the electrocatalytic activities of commercial Pt/C and 350°C annealed $\text{Pd}_4\text{Co}/\text{C}$ for the oxygen reduction reaction with Nafion-112 and -115 membranes and different catalyst loadings.

electrocatalysts to methanol can thus help to lower the cathode catalyst loading and to operate DMFCs with higher concentrations of methanol, offering cost savings and increase in overall energy density. Moreover, the cost of Pd is approximately 25% of the cost of Pt, and the replacement of Pt-based electrocatalysts by Pd-based

electrocatalysts will lower the overall system cost as a significant portion of the DMFC system cost is due to the electrocatalysts.

While Pt itself is a poor electrocatalyst for methanol oxidation, addition of hydrophilic Ru that facilitates the formation of hydroxyl groups provides good catalytic activity, although the migration of Ru from the anode to the cathode is a serious problem. Similarly, addition of other hydrophilic elements such as tin (Sn) to Pt is also known to enhance the catalytic activity for methanol oxidation. While replacement of Ru by Sn can lower the cost to some extent, replacement of Pt by other less expensive metals is desirable. Explorative research could lead to the identification of potentially low cost electrocatalysts for the methanol oxidation reaction.

As pointed out earlier, carbon corrosion under the operating conditions of DMFCs is another issue. In this regard, replacement of carbon by other conductive oxide supports may prove to be useful. Also, supporting the metal or alloy electrocatalysts on oxides could enhance the methanol oxidation kinetics by facilitating the oxidation of the CO intermediate to CO_2 . Oxide supports are being increasingly explored in recent years, and they may prove to be a viable approach to overcome the carbon corrosion problem.

MANUFACTURING CHALLENGES

The membrane-electrode assembly is a key component of a DMFC. The performance of DMFCs is highly dependent on the MEA fabrication process. There are two major MEA manufacturing processes: (1) catalyst coated substrate (CCS) method and (2) catalyst coated membrane (CCM) method.[22] In the CCS method, the catalyst layer is directly coated on the top of the substrate (such as carbon paper or carbon cloth containing the gas diffusion layer (GDL)) and then hot pressed with the membrane. In the CCM method, the catalyst is coated on the membrane and then hot pressed with the carbon cloth or carbon paper containing GDL. There are two approaches with the CCM method: (1) direct catalyst coating on the membrane (hereafter referred to as CCM) and (2) a decal transfer method (DTM).[23] However, the DTM method needs an additional transfer step, so the direct catalyst coating (CCM) on the membrane is the efficient and simple process for the continuous manufacturing of MEAs. Figure 9 compares the performances of MEAs fabricated by the CCS, CCM, and DTM methods. The CCM process offers better performance than the CCS method. Also, when the catalyst is coated on the porous substrate, a significant amount of catalyst is wasted due to the permeation of the electrocatalyst nanoparticles into the porous substrate. Thus, both from a performance and continuous manufacturing points of view, the CCM method is preferred.

However, the CCM process is complicated by the swelling of the membrane when the membrane is hydrated during the direct coating process.[24] The hydration process induces in-plane compression in the friable membrane, and the membrane creeps to relieve these stresses. To achieve stable direct coating on the membrane, the swelling problems should be controlled. Approaches with pre-swelled membranes in our laboratory appear promising, and they may prove useful to overcome this problem.

Several techniques can be employed for coating the catalyst.[25] For example, spraying, painting, and doctor blade methods are all used successfully. However, factors like coating time, reproducibility, consistency, and controllability need to be considered for continuous coating processes. Also, the procedures for the preparation of the catalyst ink slurry play an important role in controlling the particle size, surface morphology, composition, and electrocatalytic activity with direct consequences on the fuel cell performance.[26] It is important to avoid the growth of the electrocatalyst nanoparticles during the electrode fabrication procedure. Specific organic solvents and optimized procedures should be used to achieve a high degree of dispersion and to prevent particle growth during the electrode preparation processes.

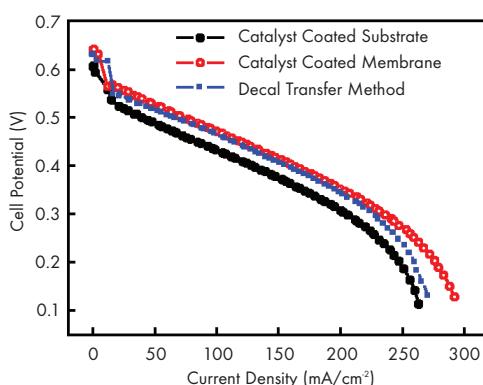


Figure 9. Comparison of the performances of MEAs fabricated by different methods.

In addition to MEAs, other components like the bipolar plates serving as current collectors play a key role in the performance of DMFCs. Graphite is generally used for bipolar plates. The graphite bipolar plates with flow channels/fields for liquid methanol and oxygen/air feed are currently fabricated by machining, which is slow and expensive. Development of alternative manufacturing processes, such as freeform fabrication methodologies, may not only increase the production rate but could also allow the design of complex and more efficient flow fields which can enhance power density.

CONCLUSIONS

Direct methanol fuel cells are appealing as a power source for a variety of DoD applications. However, their adoption is hampered by high cost, durability, and performance issues, which are linked to severe materials, manufacturing, and system challenges. Development of low-cost, more efficient materials, novel manufacturing processes, and innovative system design can enhance their commercialization prospects for DoD and consumer applications.

Design and development of new membrane materials based on aromatic polymers not only lower the membrane cost but also minimize some of the persistent problems such as methanol crossover. For example, blend membranes based on an acidic aromatic polymer and a basic aromatic polymer are found to exhibit lower methanol crossover and higher power density than Nafion-115 membrane, while lowering the cost. Similarly, Pd-based alloys with a high tolerance to methanol are found to be promising for the oxygen reduction reaction. Despite the lower intrinsic catalytic activity compared to that of Pt, the higher tolerance to methanol makes the Pd-based electrocatalysts competitive with Pt, while also allowing potentially a lower cathode catalyst loading. The cost of Pd is approximately 25% of the cost of Pt, and the replacement of Pt by Pd-based alloys can lower the DMFC cost significantly. Coupling of the new blend membranes that have suppressed methanol crossover with the Pd-based alloy electrocatalysts which have high tolerance to methanol could further reduce the problems of methanol crossover. Such a system could also allow operation with higher concentrations of methanol, offering the potential to increase the energy density compared to that achieved with Nafion and Pt-based electrocatalysts. Discovery of new low-cost, more efficient electrocatalysts for methanol oxidation could offer further gains.

Reproducible, cost-effective, continuous manufacturing of membrane-electrode assemblies is also critical for a viable commercialization of the DMFC technology. Catalyst coated membrane approach offers advantages over other methods, but the membrane swelling issue during the process needs to be addressed. Similarly, novel manufacturing approaches to fabricate bipolar plates with optimum flow fields can enhance the performance. Finally, efficient integration of the various components with adequate controls is critical to realize a DMFC system with reliable performance.

ACKNOWLEDGEMENTS

Financial support by the Office of Naval Research MURI grant No. N00014-07-1-0758 is gratefully acknowledged. The author also thanks Mr. Wen Li and Dr. In-Su Park for their assistance with the data and figures.

NOTES & REFERENCES

- * Nafion is a registered trademark of E. I. du Pont de Nemours and Company, Corporation.
- † The Pt electrocatalyst is poisoned by the methanol that permeates from the anode to the cathode through the Nafion membrane.
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